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## (54) PRESENSITISED LITHOGRAPHIC MATERIAL

- (71) We, KODAK LIMITED, a company registered under the laws of England, of Kodak House, Station Road, Hemel Hempstead, Hertfordshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to presensitised lithographic materials.
- According to the present invention there is provided a presensitised lithographic material comprising a support, a hydrophilic layer and over the hydrophilic layer a light-sensitive layer containing a polymer, said hydrophilic layer containing poly(vinyl alcohol) and/or other synthetic polymer latex or latices as a binder and the hydrolysis product of an alkyl orthosilicate.
- The light-sensitive layer in one material of this invention may be a silver halide emulsion layer (e.g. with a gelatin binder) capable of being etch-bleached after exposure and development to remove the emulsion layer in the silver areas thus making the underlying hydrophilic layer accessible to processing liquids. The resulting material has a surface consisting of areas of emulsion layer which are, or can be made, oleophilic and areas of the hydrophilic layer below. The light-sensitive layer in another such material of this invention may be a light-sensitive polymer which may be negative-working (exposed area is hardened) or positive working (exposed area becomes removable).
- Suitable light-sensitive composition for use in the presensitised printing plates of this invention are described in U.S. Patent 3,511,611 (U.K. 29409/67, Serial No. 1,191,906).
- The polyvinyl alcohol (PVA) used as the binder in the material of this invention may be of any commercial grade, e.g. 20% by weight residual acetate or less. The use of polyvinyl alcohol having an acetate content of not more than 3% by weight, e.g. 1% to 3% by weight, is preferred since this can be toughened (i.e. made resistant to rubbing) to a higher degree than layers prepared from PVA of the same molecular weight having a higher acetate content. In the Example 1 of our parent Application 806/72 (Serial No. 1,419,511), which describes and claims an image-receiving material for use in the photographic silver salt diffusion transfer process wherein the image-receiving layer contains polyvinyl alcohol as a binder (and also colloidal silica, certain inert particles and a silver precipitating agent), a very tough layer is produced. The hydrophilic layer described in Example 1 below is similar to the image-receiving layer described in Example 1 of Application 806/72 (Serial No. 1,419,511) except that it does not contain the silver precipitating agent (mild silver protein). If the PVA content in this Example is reduced by 50% or more the dry-rub resistance of the hydrophilic layer is reduced. On the other hand if the PVA content is increased by 20 to 30% the wet-rub resistance is decreased probably to an unacceptable level. An example of the polyvinyl alcohols which may be used is 'Gelvatol' 3-91 sold by Monsanto. The average molecular weight of the PVA may be from 5000 to 126000 for example.
- In fact almost any grade of PVA will work as a binder but the best results are achieved when high molecular weight, low residual acetate PVA are used. PVA containing not more than 3% by weight acetate are preferred.
- Instead of using PVA as the binder in the material of this invention, one or more other synthetic polymer latices can be used as the sole binder, or mixed with PVA. For example a latex of a copolymer of carboxylated styrene and butadiene mixed with PVA may be used. One such latex is marketed by Doverstrand Ltd. under the registered trade mark 'Revinox' 9210. Any polymer latex employed in this invention as a binder e.g. with poly (vinyl alcohol) or alone, in

[Price 33p]

the hydrophilic layer should be compatible such that coating mixture is free flowing.

5 HTEOS (hydrolysis product of tetraethylorthosilicate) is extremely hydrophilic but when used at a high concentration in the layer the HTEOS produces a very tough glass-like layer which is unsatisfactory for lithography. However, when used at a low level, preferably from 5% to 30% by weight  
10 calculated as  $\text{SiO}_2$  (=8% to 48% by weight calculated as  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), based on the dry solids content of the layer, the resulting layer is rendered tough and resistant to rubbing.

Resistance to wet rubbing is required to resist the rubbing of the plate which takes place during preparation and use of the plate when printing therefrom. Resistance to dry rubbing i.e. abrasion resistance is required to avoid the material being scratched during  
20 storage or handling before use.

Lack of wet rub resistance will cause the hydrophilic layer or parts thereof to be removed from the plate and lack of dry rub resistance, allowing scratching, shows up as  
25 black scratch lines in the printed matter.

Generally speaking the HTEOS is incorporated in the layer at the highest concentration consistent with obtaining a coating solution the viscosity of which is stable for at least 1 week. Much higher concentrations could be used but solution stability would be adversely affected. In the Examples of the invention described below, 8cc of a product obtained by hydrolyzing TEOS  
30 mixed with an equal volume of liquid is used to toughen a layer formed from 30cc of a 6.7% weight solution of polyvinyl alcohol. Hydrolysis of tetraethylorthosilicate may be effected in an acidic or basic medium. We  
35 prefer to use an acidic medium. The medium may be a mixture of ethyl alcohol and water and the acid may be an inorganic acid such as hydrochloric acid.

Whether the layer containing the HTEOS is resistant to wet rubbing can be tested simply, namely by wetting a cotton swab with water and rubbing hard by hand on the layer. When subsequently used to make a lithographic press no trace of rubbing will  
40 appear in the printed work obtained from the plate if the layer is hard enough. On the other hand, if the layer is not hard enough rubbing marks will show in the print and ink areas of the print may even be  
45 missing in the wet-rubbed parts.

The hydrophilic layer in the presentised lithographic material of this invention may also contain colloidal silica or may contain fumed silica particles or fumed alumina particles or may contain particles having an average diameter at least 200Å which are particles of titanium dioxide or other heavy metal oxide or particles of alumina or clay, said particles being inert to poly(vinyl  
50 alcohol).

The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 400Å, e.g. 200Å. Examples of such dispersion include 'Syton' (Registered Trade Mark) X-30 sold by Monsanto.

When viewed at sufficiently high magnification the fumed silica and fumed alumina particles appear to be comprised of smaller units of material linked together in the branched chain-like formation. The individual units in the 'Cab-o-Sil' brand of fumed silica have an average diameter about 120Å and the individual units of fumed alumina have an average diameter of about 300Å. The number of smaller units in the particles is usually at least 5 and normally higher although normally less than 100. These branched chain-like particles when coated alone do not cohere to form a layer and they are much less dense than discrete spherical particles of the same chemical composition.

The inert particles of larger size than the colloidal silica other than the fumed silica and fumed alumina particles which may be employed in this invention may be particles of an average diameter of at least 200Å, e.g. from 250Å up to 10000Å, e.g. from 250Å to 1000Å, preferably 500Å to 1000Å. These particles may be ordinary aluminas or heavy metal oxides e.g. titanium dioxide or clays.

These larger particles help to maintain the porosity of the layer which tends to be reduced by the HTEOS. Preferably, fumed alumina or fumed silica is used as the source of the larger particles; they mix easily with the other components of the layer. Fumed silicas and aluminas can be made by flame hydrolysis of silicon tetrachloride or aluminium trichloride respectively. Temperatures of about 1100°C are employed.

By inert particles we mean, in this specification and claims that the particles have little, if any, hardening effect on the PVA.

In the presentised lithographic material of this invention the hydrophilic layer preferably contains:

(a) poly(vinyl alcohol) as a binder; 115  
(b) colloidal silica;

(c) fumed silica, fumed alumina particles or other inert (a herein defined) particles which particles have a larger average diameter than the colloidal silica particles; and 120

(d) the hydrolysis product of an alkyl orthosilicate, in a ratio by weight of the  $\text{SiO}_2$  content of component (b) plus component (c) plus the  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  content of (d) to component (a) of at least 9:5 and said hydrophilic layer having been coated at a pH not less than 6.5. 125

In this preferred material the PVA pre- 130

ferably has an acetate content of not more than 3% by weight.

Preferably also, in this material, component (c) comprises fumed silica particles having a branched chain-like structure in which the individual units have an average diameter about 120Å or fumed alumina particles having a branched chain-like structure in which the individual units have an average diameter about 300Å.

Alternatively, the inert larger particles may be particles of titanium dioxide.

If colloidal silica having an average diameter >200Å, e.g. 400Å is used then the average diameter of any inert particles used therewith is higher, e.g. up to 1000Å or higher.

The total thickness of the hydrophilic layer in the material of this invention is preferably low.

A suitable thickness was obtained by coating the composition described in the Example 1 below at a rate of 20 ccs per square metre.

The composition which is coated to produce the hydrophilic layer in the presensitised material of this invention should be free flowing and the pH of the composition containing components (a), (b), (c) and (d) defined above not less than 6.5 preferably from 7 to 9.

The amounts of each component in the hydrophilic layer of the material of the present invention may be varied provided the total solids including HTEOS solids to binder ratio does not vary too much, and the physical characteristics and shelf life of the layers are not drastically impaired.

In the hydrophilic layer of the presensitised material of the invention from 10% to 30% of SiO<sub>2</sub> as colloidal silica and from 10% to 40% of SiO<sub>2</sub> as fumed silica may be employed, the percentages being by weight based on the weight of dry solids in the layer.

The following table indicates levels of additions to the PVA found to yield satisfactory results for the hydrophilic layer.

TABLE

	Colloidal silica+ * HTEOS : PVA by weight	Matting agent (said larger particles) : PVA
55 <i>Broad ranges</i>	1:2 to 7:1	5:2 to zero matting agent (Too much makes the layer too porous).
60 <i>Preferred ranges</i>		Example 1 7:4
HTEOS+Colloidal silica : PVA	1:1 to 4:1	
e.g. ... ..	2:1	
e.g. Example 4 ... ..	3:1	
HTEOS alone: PVA ... ..	2:3 to 2:1	
e.g. Example 4 ... ..	1:1	
65 * as SiO <sub>2</sub> .2H <sub>2</sub> O		

(In the Table above, the references to 'colloidal silica' means SiO<sub>2</sub> although in actuality the particles are composed of hydrated silica SiO<sub>2</sub>.xH<sub>2</sub>O where 'x' is not known with precision).

The preferred ranges show that if the relative proportion of colloidal silica to HTEOS in the mixture is reduced then the total ratio of HTEOS plus colloidal silica to PVA may also be reduced to approach 2:3. On the other hand if the proportion of colloidal silica is increased then the total ratio of HTEOS+colloidal silica to PVA is likely to be increased.

If a less tough hydrophilic layer is required a lower proportion of HTEOS, based on the PVA, may be used although it should be noted that if the proportion is lowered too much without increasing the proportion of other hardeners (organic or inorganic) the PVA will be insufficiently hardened and

the presensitised layer will be liable to scuff off.

We have found that gradually increasing the amount of the PVA added to the layer (from a point necessary to achieve binder action) causes a rapid increase in the wet-rub resistance of the layer at first, then a much slower increase and finally a falling off in resistance.

On the other hand gradual increase in the amount of PVA added to the layer causes only a slow increase in dry-rub resistance (when resistance to wet rubbing is increasing rapidly) and often only reaches the maximum when the wet-rub resistance has fallen substantially.

In the present invention the amount of PVA employed is preferably such that the dry-rub resistance, measured as defined below, has reached a high acceptable value consistent with achieving the minimum fall (from the maximum) in value of wet rub resistance. A layer more resistant to wet-rubbing can be obtained by reducing the quantity of PVA added, e.g. by reducing the quantity by 10%, but will result in some loss of dry-rub resistance.

Comparisons of the dry rub (abrasion) resistance of various materials according to the invention may be made by testing in an apparatus comprising a vertically weighted glazier's diamond. The material is held down by vacuum on a flat bed and drawn slowly under the diamond. The weight required to scratch the layers down to the support is a measure of the abrasion resistance. Such a scratch is detected by an ink-line appearing in the printed work.

The material of the present invention may comprise a hydrophobic support which has been treated to provide a surface to which the hydrophilic layer can be applied and adheres. Examples of such supports are polyethylene or polyolefin (e.g. polyethylene) coated paper, the polyethylene or polyolefin having been subjected to a corona discharge, photographic film base e.g. poly(ethylene terephthalate), cellulose acetate film base, plastics having a metal layer or deposit thereon which has been treated to provide said surface or a metal support itself, e.g. Al which has been treated to provide the required surface for the coating thereon to adhere to.

For cheapness the preferred base for the presensitised materials of this invention is high wet-strength paper, preferably paper having a developer-resistant polymer coating on both sides e.g. a polyethylene coating on both sides. The polyethylene coating on which the hydrophilic layer is to be coated is, of course, given a preliminary corona treatment. Polyethylene terephthalate bases may be employed e.g. 'Estar' bases. These give longer running plates but are more expensive. Aluminium foil may also be used as a base provided it is first thoroughly cleaned e.g. with an alkali and alcohol. The aluminium plays not part in image formation nor does it require an anodized surface.

The following are examples of the hydrophilic layers useful in making the presensitised materials of the invention.

#### EXAMPLE 1

A coating composition was prepared by mixing the following components under high shear for two minutes. (Percentages are by weight.)

1. Fumed silica (Cabot Carbon, Cab-O-Sil M-5) 35 ccs of a 10% dispersion

in water. Each fumed silica particle contains from 10—100 units of average diameter 120Å.

2. Polyvinyl alcohol (Monsanto, Gelvatol 3-91) 30 ccs of a 6.7% solution in water. This poly(vinyl alcohol) has a residual acetate content of 3% and a high molecular weight indicated by '91'. 70
3. Colloidal silica of average diameter 200Å (Monsanto Syton X-30) 7ccs of a 30% solids dispersion. The word 'Monsanto' is a Registered Trade Mark). 75
4. 8 cc Hydrolyzed tetraethyl orthosilicate (Eastman 4203). 80
5. 16 ccs water.

A polyethylene-coated paper base as described in Example 1 of U.K. Specification 1,111,684 was subbed very thinly with gelatin after electron bombardment and the above composition was coated thereon at the rate of 20 ccs/M<sup>2</sup>. This coating constitutes the hydrophilic layer. 90

#### EXAMPLE 2

Example 1 was repeated with the modification that a poly(vinyl alcohol) having a lower acetate content was used in the first-coated composition forming the hydrophilic layer in accordance with the invention. The poly(vinyl alcohol) employed is identified commercially as Gelvatol PVA 1-90. This PVA has a residual acetate content of 1% and a high molecular weight (indicated by '90'). 95

#### EXAMPLE 3

Example 1 was repeated with the variation that the fumed silica was omitted from the first-coated composition forming the hydrophilic layer. 105

#### EXAMPLE 4

As Example 1 except the coating composition for the hydrophilic layer was obtained by mixing:— 110

- |                     |     |     |       |     |
|---------------------|-----|-----|-------|-----|
| (1) PVA (1-90) 6.7% | ... | ... | 30 cc |     |
| (2) hyd. TEOS       | ... | ... | 8 cc  | 115 |
| (3) water           | ... | ... | 36 cc |     |

#### EXAMPLE 5

The above Examples were repeated with the variation that the gelatin subbing layer was omitted in each case. 120

In the above Examples the pH of each coating composition containing colloidal silica was about 8.

In the above Examples the percentages are on the following bases: 125

'Cab-O-Sil'	weight/volume
poly(vinyl alcohol) (PVA)	weight/volume
colloidal silica	weight/weight of dispersion 130

In the above Examples the reference to 'solids' in the dispersion constituting the 'Syton' means  $\text{SiO}_2$ .

In the above Examples the tetraethyl orthosilicate is hydrolysed by addition of an equal volume of a 1:1 mixture of water and industrial methylated spirits containing a catalytic amount of concentrated hydrochloric acid (approximately 1 drop per 30 cc of mixture). The temperature rises quickly over a period of 2 to 3 minutes. The solution is then allowed to cool. Hydrolysis is then sufficient. The hydrolysed chemical should be used within 24 hours for best results.

#### WHAT WE CLAIM IS:—

1. A presensitised lithographic material comprising a support, a hydrophilic layer and over the hydrophilic layer a light-sensitive layer containing a polymer, said hydrophilic layer containing poly(vinyl alcohol) and/or other synthetic polymer latex or latices as a binder and the hydrolysis product of an alkyl orthosilicate.

2. A material according to Claim 1, the ratio by weight of the  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  content of said hydrolysis product to poly(vinyl alcohol) in said hydrophilic layer being from 2:3 to 2:1.

3. A material according to Claim 1, said hydrophilic layer also containing colloidal silica.

4. A material according to Claim 3, the ratio by weight of the  $\text{SiO}_2$  content of the colloidal silica plus the  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  content of said hydrolysis product to poly(vinyl alcohol) in said hydrophilic layer being from 1:1 to 4:1.

5. A material according to Claim 1 or 2, said hydrophilic layer also containing fumed silica particles or fumed alumina particles, said particles having a branched chain-like structure and being inert as herein defined.

6. A material according to Claim 1 or 2, said hydrophilic layer also containing particles of titanium dioxide or other heavy metal oxide, said particles having an average diameter at least 200Å and being inert as herein defined.

7. A material according to Claim 1 or 2, said hydrophilic layer also containing particles of alumina or clay, said particles having an average diameter at least 200Å and being inert as herein defined.

8. A material according to Claim 5, 6 or 7, the ratio by weight of said particles

to poly(vinyl alcohol) being not more than 5:2.

9. A material according to Claim 1, said hydrophilic layer containing:

(a) poly(vinyl alcohol) as a binder; 65  
(b) colloidal silica;

(c) fumed silica, fumed alumina particles or other inert (a herein defined) particles which particles have a larger average diameter than the colloidal silica particles; and 70

(d) the hydrolysis product of an alkyl orthosilicate, in a ratio by weight of the  $\text{SiO}_2$  content of component (b) plus component (c) plus the  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  content of component (d) to component (a) of at least 9:5 and said hydrophilic layer having been coated at a pH not less than 6.5. 75

10. A material according to Claim 9 wherein the poly(vinyl alcohol) has an acetate content of not more than 3% by weight. 80

11. A material according to Claim 9 or 10 wherein component (c) comprises fumed silica particles having a branched chain-like structure in which the individual units have an average diameter of about 120Å. 85

12. A material according to Claim 9 or 10 wherein component (c) comprises fumed alumina particles having a branched chain-like structure in which the individual units have an average diameter of about 300Å. 90

13. A material according to Claim 9 or 10 wherein said inert larger particles are particles of titanium dioxide. 95

14. A material according to any of the preceding claims, said hydrophilic layer having been coated at a pH from 7 to 9.

15. A material according to any of the preceding Claims said hydrolysis product having been obtained by hydrolysis of tetraethyl orthosilicate in an acidic medium. 100

16. A material according to any of the preceding Claims wherein the proportion of poly(vinyl alcohol) in said hydrophilic layer is such that the dry-rub resistance, determined as herein defined, has reached a high acceptable value consistent with achieving minimum fall from the maximum of wet-rub resistance. 105

17. A material according to any of the preceding Claims wherein the support is composed of a hydrophobic material which has been treated to provide a surface to which the hydrophilic layer adheres. 110

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